Synchronized Oscillations of Dimers in Bi-phasic Charged fd-virus Suspensions

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Micron-sized colloidal spheres that are dispersed in an isotropic-nematic bi-phasic host suspension of charged rods (fd-virus particles) are shown to spontaneously form dimers, which exhibit a synchronized oscillatory motion. Dimer formation is not observed in mono-phase of isotropic and nematic suspensions. The synchronized oscillations of dimers are connected to the inhomogeneous state of the host suspension of charged rods (fd-viruses) where nematic domains are in coexistence with isotropic regions. The synchronization of oscillations occurs in bulk states, in the absence of an external field. With a low field strength of an applied electric field, the synchronization is rather reduced, but it recovers again when the field is turned off. *In this Letter, we report this observation as an example of the strange attractor, occurred in the mixture of PS-dimers in an isotropic-nematic coexistence biphasic fd-virus network. Furthermore, we highlight the synchronization of PS-dimer oscillation is the result of a global bifurcation diagram, driven by a delicate balance between the short-attractive "twisted" interaction of PS-dimers and long ranged electrostatic repulsive interactions of charged fd-rods.* The interest is then the local enhancement of "twist-nematic" elasticity in reorienting of the dimer oscillations. The analysis of image-time correlations are provided with the data movies and Fourier transforms of averaged orientations for the synchronized oscillations of dimers in biphasic I-N coexistence concentration of charged fd-virus suspensions.

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When a system exhibits two minima in its free energy as a function of a given order parameter with similar depths, which are separated by a small energy barrier of at most a few times the thermal energy, it will persistently switch between the two corresponding states. In a multi-dimensional order-parameter space, the existence of two free energy minima may result in a so-called strange attractor where the system switches between the free energy minima through quasi-stochastic orbits in the order-parameter space [1]. A biological example that exhibits this behavior is the dimer-oscillation in Hes/Her dimer-proteins of zebrafish, where synchronized segmental oscillations serve as a clock [2]. In this paper, we describe a similar behavior observed in a dispersion of colloidal spheres in a host suspension of charged colloidal rods in the isotropic-nematic biphasic concentration. The spontaneous formation of polystyrene (PS) dimers occurs on dispersing single PS spheres in an isotropic-nematic biphasic phase of charged fd-virus particles, and surprisingly synchronized oscillation appears with reorientation of dimer oscillations. However, the spontaneous formation of dimers is not observed in the mono-phase of isotropic or nematic suspensions of fd-virus particles. Domain boundaries thus play an essential role in the spontaneous formation of PS-dimers. A possible mechanism for the formation of dimers and the observed synchronization of PS-dimer oscillations are possibly due to the above mentioned existence of two free energy minima for a dimer as a function of the distance between the two spheres within the dimer, as mediated through the interaction of two spheres within the nematic domain boundaries. The degree of synchronization is observed to reduced by upon applying a weak electric field, which has little effect on single PS-sphere dynamics. The synchronized motion is fully recovered by switching off the electric field.

The polystyrene (PS) microspheres are prepared by dispersion polymerization of purified styrene monomer, with polyvinylpyrrolidone (Molecular weight $Mw \sim 55Kg/mol$), 2-azobisisobutyronitrile and ethanol used as a stabilizer, initiator and dispersion medium, respectively [3]. The inset of Fig.1a shows a scanning electron micrograph (SEM) of the PS spheres, which have a diameter of $1.5\,\mu m$. The negatively charged PS spheres in powder form are dispersed in a low ionic strength (0.032 mM) Tris/HCl buffer. Dynamic light scattering correlation functions on dilute dispersions of PS spheres (without the fd-virus particles) are shown in Fig.1a, both in the absence and presence of an external electric field. Here, the wavelength of the He/Ne laser light is $633\,nm$ (JDS Uniphase Model 1145P), and an ALV-5000/EPP multiple tau digital real time correlator is used. The scattering angle corresponds to a length scale of $2.7\,\mu m$, so that displacements of the PS-spheres are probed over distances that are comparable to their own size [4]. The peak in these correlation functions is due to heterodyning. As can be seen from these correlation functions, the typical weak electric field strengths that we apply in the present study (less than 3 V/mm) have no significant effect on the dynamics of single PS -spheres. The effect of electric fields on the dynamics of PS spheres at much higher field strength has been studied before as electrorheological fluids, where dielectric polarization is important [5]. In the presence of such high field strengths (typ-

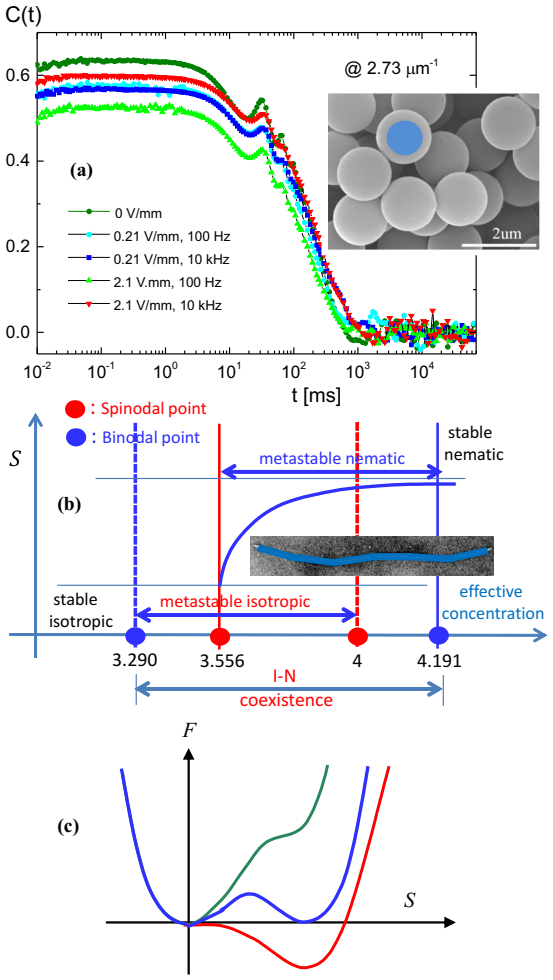

Figure 1: (a) In-situ electric-field dynamic light scattering of polymerized polystyrene (PS) spheres in a low ionic strength of Tris/HCl buffer solution (of 0.032 mM), for various field-conditions at a fixed scattering wavevector. The inset is the scanning electron micrograph of PS sphere. (b) The brief sketch of an order parameter versus concentration phase diagram of the host system of colloidal rods (of fd-viruses), where two spinodal and binodal points are indicated with the isotropic-nematic (I-N) coexistence concentration. (c) Corresponding free energy function as a function of order parameter for rod-suspensions: I-N biphasic state (blue line) is under instability between lower (green line) and upper binodal (red line) concentrations.

ically larger than 100 V/mm), dielectric polarization of the interface between the particles and the solvent leads to PS-sphere inter-particle interactions give rise to the formation of strings. However, for the weak fields applied in the present study, there is no significant effect on the behavior of the PS-sphere dispersions.

Also for host system of charged rods in which the PS-spheres are embedded, suspensions of fd-virus particles are used. Fd-virus particles are highly charged (a total charge of 10.000 elementary charges), consisting of helical DNA strand, covered with about 2700 coat proteins [7]. The length of a fd-virus particle is $880\,nm$, and the core thickness is $6.8\,nm$, with the persistence length of $2200 - 2500\,nm$ (see the inset of Fig.1b). The ionic strength in the present experiments is far low, as $0.032\,mM$, corresponding to a relatively large Debye screening length of $54\,nm$ [10]. At this low ionic strength, the effective diameter that measures the range of electrostatic interactions is a few times larger than the bare core diameter [8]. For lowering the ionic strength of suspension of highly charged fd-virus, different phase longer electrostatic interactions are exhibited in the phase behaviors [9]. At the very low ionic strength used here, the isotropic-nematic phase boundaries are located at relatively quite low fd-concentrations [10], while no sedimentation occurs of nematic domains in the bi-phasic region over a time span of many hours. PS is used as a tracer method, meaning that they are much diluted as compared to the suspensions of fd- virus so that PS is expected to be not interacting themselves in the medium of fd-virus networks. Thus the phase diagram of fd-virus should not be influenced by the presence of PS-particles. This is the reason that the Brownian motion of PS is seen not only in an isotropic-, but also in a nematic fd-virus network.

The structure and dynamical correlations of diluted suspension of charged fd-virus rods are studied before by Monte Carlo simulations [11], and Brownian dynamics simulation [12], as well as the dynamics of isotropic-nematic and shear-induced I-N transition [13], and the stabilization of chaotic state under shear stress [14]. However, as far as we know, there is no yet direct observation that experimentally found dimer-oscillations in the bifurcation diagram of an isotropic-nematic (I-N) coexistence concentration, as resulting formation of a strange attractor. Fig.1b is the brief sketch of an order parameter versus a concentration phase diagram of colloidal rods (of fd-viruses), where two spinodal and binodal points are indicated with the I-N coexistence concentration. Here the effective concentration is estimated by Onsager's theory [8], independent of ionic strength. The resulting long-ranged electrostatic interactions lead to an effective potential trap such that for each particle is within the energy landscape set by neighboring particles. For elongated particles, nonlinear self- consistent Smoluchowski equation for orientational distributions can be described by the Maier-Saupe model, where non-equilibrium free energy and entropy are estimated for the time-evolution of an order parameter [15]. Free energy is shown as a function of order parameter in Fig.1c, which now indicates the global minimum is corresponding to the I-N bistable state order parameter. Such slightly perturbed free energy function is shown for a lower binodal and upper binodal concentrations in Fig.1c. The effect of a high electric field on the suspension of polystyrene alone is reported by a dynamic light scattering such that the decay rates are proportional to the viscosity changes in

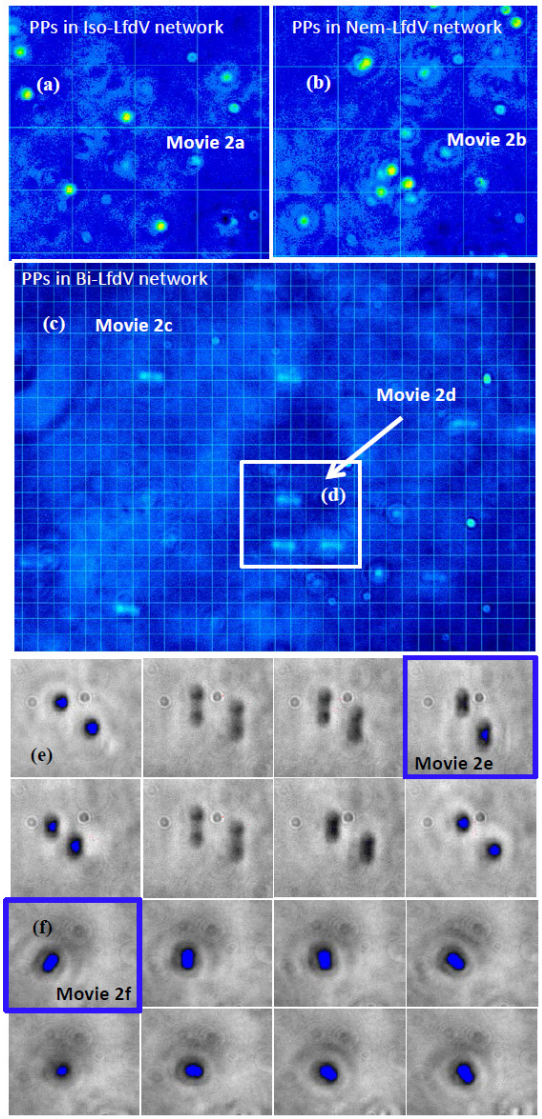

Figure 2: Optical morphology and movie data for Brownian motion of polymerized polystyrene (PS) spheres in a monophase of (a) an isotropic fd-virus network, and (b) in nematic fd-virus network. (c) and (d) are shown for synchronization of PS-dimer oscillations in I-N coexistent biphasic fd-virus network. (e) Few temporal snap shots of different orientations of dimer oscillations in bulk state, and (f) the rotations of dimers without oscillations in thin cell thickness. Blue color is coded for the lower part of the image, and the time step is 0.25s. Supplementary movies (Movie 2a, 2b, 2c, 2d, 2e, and 2f) are provided.

the presence of an electric field [5]. PS is one of candidates of electrorheological fluid, where the dispersion is consist of uniform dielectric spheres. In the presence an electric field, polarization occur at the interface between particles and the solvent. Dilute suspensions of permanent electric dipole moments and electric polarizability to an applied electric field are also shown nonlinear relaxation of time-dependent polarizaibity, and the optical susceptibility. However, at a low electric field strength, there are no significant differences on the intensity-auto correlation functions (see Fig.1a), as compared to the absence of an external electric field. The oscillation of a small scattering amplitude appears at roughly in the time window of 35-40 ms, which is similar ranges of relaxation time of the host system of charged fd-virus for an isotropic-nematic coexistence concentration [4].

In the absence of an external electric field, the morphologies of mixture of charged PS spheres in the isotropic, nematic, and isotopic-nematic (I-N) coexistence biphasic rod-networks (for a fd concentration of $1.0\,mg/ml$) are shown with the optical morphology and corresponding movie data (Movie2a, Moive2b, Movie2c) in Fig.2a, b, and c, respectively. First of all, Brownian motions of single PS spheres (of 1.5 um diameter) are observed in the monophase of host system, either in an isotropic (in a) or the nematic fd-rod network (in b). *However, for an I-N biphasic host of fd-rod network (in c), not only dimers of PS spheres are formed with oscillations, but also vivid motions of synchronized dimer-oscillations are appeared, whose visualization can be seen in the Movie 2c and 2d.*, as the distance between two PS in the dimer is oscillating, and this oscillation is synchronized for all the dimers in solution. The synchronization of PS-dimer oscillations occurs only in a bulk state (with the cell thickness of $1.0\,mm$ thick). The direct visualization of few snap shots of different bulk reorientations of two neighboring PS-dimers in the biphasic fd-virus networks are provided in Fig.2e.

For lowering the sample thickness (of $0.5\,mm$ thick cell) in the same biphasic host concentration, dimer oscillations are not seen, but only free rotations of "tightly" packed dimers are detected, consisting of two attached PS spheres, without a separation, in Fig.2f. It confirms that the existence of dimer oscillations is related to the bulk isotropic-nematic domains, as a global bifurcation process. The transient reorientations of PS-dimer oscillation of biphasic fd-rod networks are presented in Fig.3a-c, with their morphological snap shots, on the right side, in which those orientations occur instantaneously in bulk state. A reason for the formation of PS-dimers in the biphasic fd-rod network is due to the spatial coherence length of charged fd-virus suspensions is found to be the minimum length scale at an isotropic-nematic coexistence concentration. It may indicate that there will be a 'local" enhancement of "twist"-nematic elasticity play a role, in N*-phase, which is now briefly sketched in the middle of Fig.3d. The anisotropic deformation of director field is depicted as the I-N biphasic fd-rod network, and related to the "strange attractor" of biphasic rod-network (of Iso + Nem). Thus the strange attractor is shown as torus-tube shape, not the butterfly-shape that can be related the latter cases of lower and upper binodal concentration. Also, at a higher field amplitude, sudden changes of the flux of PS-dimers are seen in the

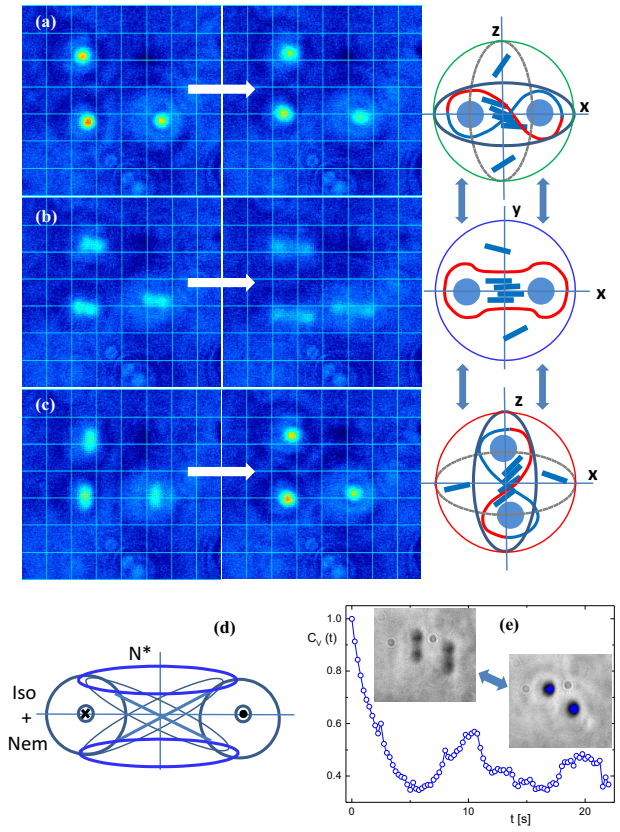

Figure 3: (a)-(c): Few snap shots and possible schemes of synchronized dimer oscillations: (a) Dimers formed in the absence of external field, but soon oscillates to a planar state on x-y direction on the right panel. (b) Fully stretched in the x-y plane, and (c) local orientation changes to z-axis, before it returns to the state (a). (d) The brief sketch of strange attractor, where the local twist-nematic, N*-phase may exist between dimer oscillations, within nematic domains in isotropic background. (e) An image-time correlation function obtained from the movie data of Movie 2e, with two distinguishable con?gurations of dimer orientations.

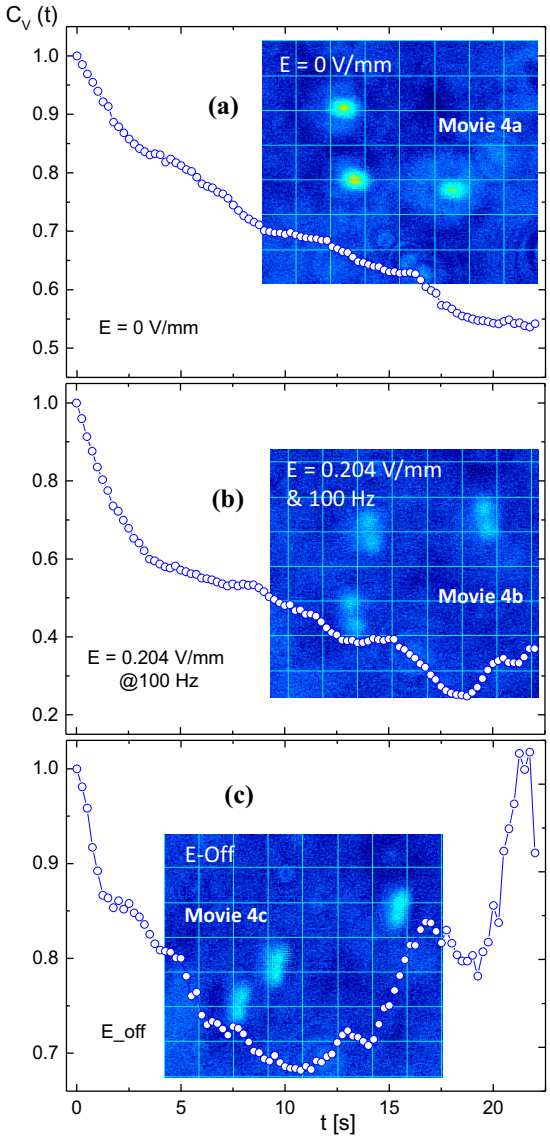

Figure 4: Image-time correlation functions and the movie data, performed in different electric field conditions: (a) 0 V/mm, (b) 0.204 V/mm and 100 Hz, and (c) turning off the electric field. Supplementary movies (Movie 4a, 4b, and 4c) are provided.

periodic manner (of larger times of few tens of sec.) with the reversed flow due to the electric polarization at a low salinity [6].

The quantification of kinetics of dimer oscillations are then performed by an image-time correlation function [4], obtained from the collection of time-lapsed images, as follows: Let $I(t)$ be the instantaneous transmitted intensity detected by a given pixel of the CCD camera (AxioCam Color A12-312 CCD camera, with a chip of 1300×1030 pixels). From time traces recorded for all these pixels, the image correlation function $C_V(t)$ is computed, which is defined as,

$$C_V(t) = \frac{< (I(t) - < I(t) >)\,(I(0) - < I(0) >) >}{< (I(0) - < I(0) >)^2 >}, \quad (1)$$

where the brackets $< \cdots >$ denote averaging over all CCD-camera pixels. Each single image in a time trace is used to construct an image correlation function, from the region of interest as 300×300 pixels. The above definition of the image time correlation function is reminiscent of the intensity correlation function as obtained from dynamic light scattering, except that the intensity here is not a scattered intensity but the transmitted intensity through the two crossed polarizers. Details of an image-time correlation spectroscopy can be found in ref.[4]. Two particular distinguishable configurations of PS-dimer oscillation are shown in Fig.3e, with an image-time correlation function, obtained from the time-lapsed images of the movie data of Movie 2e: One is the fully stretched in planar orientation, and the other is "reoriented" towards vertical (as "stand-up") orientation. Fur-

ther analysis on the image-time correlations for different electric-field conditions are also shown, with corresponding movie data in Fig.4: In the absence of electric field, rather slower decay rate of different steps of dimer oscillation is appeared in Fig.4a, however as soon as a low electric field is applied, in Fig.4b, a fast decay occurs immediately and progresses further to a lower value for different states of synchronized dimer oscillations. The intriguing fact is when the external electric field is turned off, the image-time correlation functions are increased again in Fig.4c. This means that the PS-dimer oscillations in a biphasic fd-rod network are fundamentally determined by the stability of a coexistence concentration, set by a thermodynamic equilibrium, and the synchronization is occurred in the collective motions of the I-N biphasic phase.

Further check on reorientation of synchronization of these dimer oscillations is done by Fourier-space images that are generated in time, in Fig.5a, and b, for larger field of views (see the dimension of Fig.2c). Typical Fourier transformed (FT) images are shown in Fig.5c, for turning off the field, both four edged circles and the center indicate reorientations of PS-dimer themselves in a biphasic host of fd-rod network. Here, note that not only the center of FT images contains anisotropic distributions, but also it reorients locally in time, depicted in the separate view of Movie 5d in Fig.5c. Few snap shots of the FT image of center (in Fig.5c and d) are provided in Fig.5e. Similar features exist in both absence and presence of an electric fields, in Fig.5a and b, respectively.

To brief summarize synchronized oscillations of PS-dimers in biphasic charged fd-rods: (i) This is the first time the strange attractor is visualized in the mixture of PS-spheres in the host of isotropic-nematic coexistent biphasic charged fd-rod networks, not in the monophase of isotropic (and nematic) phase. The PS-spheres are bounded with the charged fd-rods effectively such that initially different two states of order parameter are needed to form the stable PS-dimers. (ii) With a weak perturbation of an external electric field, the synchronization of dimer oscillations seems to be somewhat constrained, but not much affected by low electric fields, only reduced to a moderate separation distance. (iii) When the field is turned off, the synchronization recovers again, mimicking the equilibrium state of dimer oscillations. Thus the synchronization is driven by a complete global state of 'blurry' nematic-domains in an isotopic background, which is similar nature of the field-induced dynamic states [16], where "transient' order parameter kinetics vary in local space and time in the I-N coexistence concentration. (iv) The synchronization is further visualized by Fourier transforms of dimer oscillations, showing coexistence orientations of isotropic and anisotropic distributions in lager field of views of Fig.5. *Since, there is no formation of dimers in the monophase of an isotropic and nematic-network, the synchronized*

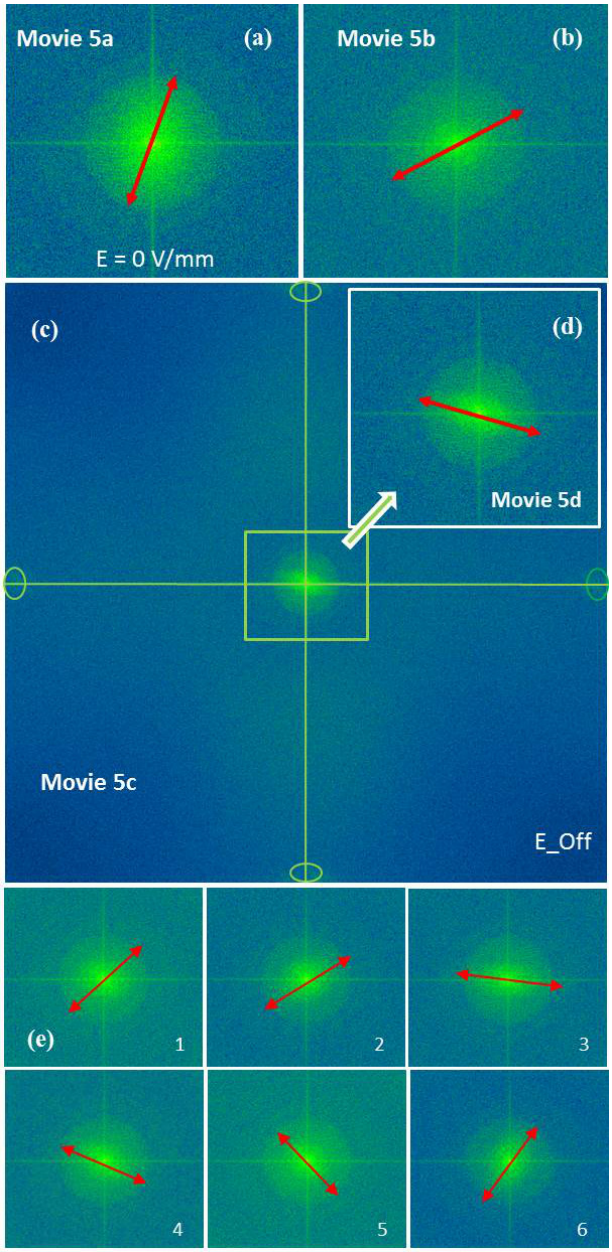

Figure 5: Fourier transforms of different electric field conditions: (a) 0 V/mm, (b) 0.204 V/mm and 100 Hz, (c)-(d): Turing off the electric field. (e) Few snap shots of di?erent orientations for turning off the field, with a time step of 0.5s. The red arrow indicates the average axis of an orientation. Supplementary movies (Movie 5a, 5b, 5c, and 5d) are provided.

PS-dimer oscillations are purely result of an energy barrier that is bounded by the effective interaction of PS-dimers in the neighbors of isotropic-nematic coexistence charged fd-rod networks.

Therefore, it is quite intriguing demonstration to show the local short-ranged attraction of two charged PS-spheres forming a dimer with oscillations, which is assisted by "twist" elasticity of charged fd-rods between

PS-dimers. The synchronization is then controlled by globally repulsive nature of electrostatic interactions in the isotropic-nematic biphasic network of charged fd-viruses. The short ranged attraction of PS-dimers are then the consequence of minimized free energy barrier in the I-N biphasic concentration, less by direct interaction of PS-sphere and fd-rods. We hope this observation is useful to provide some aspect of effective electrostatic interactions of charged complex system of spheres in the host of I-N biphasic rod networks, and furthermore to design novel microscopic motors in demixing complex fluids.

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